

## CERTIFICATE OF GRANT OF PATENT

In accordance with Section 24(2) of the Patents Act, 1977, it is hereby certified that a patent having the specification No 2298713 has been granted to Willett International Limited, in respect of an invention disclosed in an application for that patent having a date of filing of 7 March 1996 being an invention for "Method and composition"

Dated this Fifteenth day of December 1999

sown him to

Willett International Limited c/o Dummett Copp 25 The Square Martlesham Heath IPSWICH Suffolk IP5 3SL A. BRIMELOW

Comptroller-General of Patents,

Designs and Trade Marks.

UNITED KINGDOM PATENT OFFICE



# (12) UK Patent (19) GB(11) 2 298 713(13) B

(54) Title of Invention

### Method and composition

- (51) INT CL<sup>6</sup>; G01N 33/32 21/25 21/84
- (21) Application No 9604829.3
- (22) Date of filing 07.03.1996
- (30) Priority Data
  - (31) 9504495
  - (32) 07.03.1995
  - (33) GB
- (43) Application published 11.09.1996
- (45) Patent published 15.12.1999
- (52) Domestic classification (Edition Q) G1A AA4 AA6 AG6 AG9 AMK AR6 AR7 AT2 AT20 AT21 AT3 U1S S1416 S2236
- (56) Documents cited EP0083062 A2 EP0016339 A1 WO91/08556 A1 US4244741 A
- (58) Field of search

As for published application 2298713 A viz: UK CL(Edition O) B6A ATC, G1A ACDL AMBP AMBX AMHL AMK INT CL' C09D 11/02, G01J 3/427 3/51, G01N 21/31 21/35 21/91 33/26 33/32, G07D 7/00 Online database: WPI updated as appropriate

- (72) Inventor(s)

  Dennis Camilleri
- (73) Proprietor(s)
  Willett International Limited

(Incorporated in the United Kingdom)

- 3 Cronin Road Weldon South Industrial Estate Corby Northants NN18 8AQ United Kingdom
- (74) Agent and/or
  Address for Service
  Dummett Copp
  25 The Square
  Martlesham Heath
  Ipswich
  Suffolk
  IP5 3SL
  United Kingdom

TITLE: METHOD AND COMPOSITION

The present invention relates to a method and composition, notably to a method for verifying the identity of an ink used in a printing process.

### BACKGROUND TO THE INVENTION:

5

10

15

20

25

30

35

The ink used in a printer is carefully formulated to reflect the operating characteristics of that printer and often a specific ink composition will not be suitable for use in another design or type of printer. Thus, ink jet printers operate by forming discrete droplets of the ink which are jetted onto a substrate to apply individual droplets of ink to the substrate. In order that the flight of the droplets is consistent from one droplet to the other, the jetting characteristics of the ink must remain substantially constant and must be matched to the nozzle orifice geometry and the mechanism by which the droplets are formed. characteristics are dictated by, inter alia, the viscosity, surface tension and volatility of the ingredients, as well as the relative proportions of the ingredients. result, the use of inks other than those specified by the equipment manufacturer will often result in imperfect operation of the printer and, in extreme cases, physical damage to the seals and other parts of the ink jet printer. Similarly, inks for use in gravure, flexographic, litho and other forms of printing process have been formulated to meet the specific operating conditions of that type of printing process or of a specific printing apparatus.

Notwithstanding this, operators of printers often attempt to use inks from other manufacturers or suppliers where it seems that there is economic advantage in doing so. Problems may then arise with the operation of the printer

- .--

using such alternative inks. The original manufacturer may have given warranties and maintenance obligations to a purchaser of the printer based upon the use of his specified inks. If damage or imperfect operation of the printer arises, the manufacturer will often have no evidence to show that the use of a non-authorised ink as opposed to a mechanical or design fault in the equipment has caused the damage or malfunction.

To date no reliable means exists for determining whether a printer has been operated using a non-authorised ink.

It has been proposed to incorporate a material which absorbs infra red (IR) radiation into an ink composition so as to be able to detect whether the ink has been applied to a substrate or not by detecting the reflectance or absorption of IR radiation applied to the printed image. enable the operator to detect whether or not an containing such an IR absorber is present in the image. However, problems arise in accurately identifying that specific IR absorber against the background absorbence or reflectance of the desired IR radiation by other components of the ink composition and/or the substrate onto which the ink has been printed. Thus, the optical properties of the ingredients in an ink composition are liable to fluctuate, since these have not been criteria which have been the subject of control during the operation of a printer or which have not been considered relevant in the selection of ingredients for use in the ink compositions. Furthermore, it will be necessary to compensate for the optical effects of the substrate onto which the ink has been printed and for any background signal noise or extraneous light which may affect the observation of any optical effect the IR absorber may have on any sensor used to detect it.

5

15

20

25

30

It has been proposed in US Patent 4 567 370 to incorporate a Ultra Violet (UV) radiation emitting material in an ink composition and to detect the presence of that material in order to verify the authenticity of the ink by exciting the material with high intensity UV radiation. This causes the material to emit radiation at two discrete narrow band wave lengths which are detected using appropriate means. If both required wave lengths are detected, then the ink is authentic; if none or only one wave length is detected, then the ink is not authentic. However, this proposal requires the use of materials which emit radiation at specific wave lengths and the use of high intensity UV radiation to excite the material, which limits the applicability of the process and increases the cost and complexity of the equipment required.

We have found that the above problems can be reduced to an acceptable extent by monitoring the reflectance and/or absorption of radiation at two different wave lengths within a specified wave length band width and taking a ratio of the observed levels of the radiation or absorption at each wave The ratio of the levels minimises the effect of length. variation in the signal from the substrate as opposed to the ink and of any background signal noise and is remarkably consistent over a wide range of ink compositions as identifying the shape of the reflectance/absorption spectral pattern of that material. It is not necessary to excite a lumiphor to emit specific wave length radiation and the ink can be illuminated using a wide band wave length white light light source rather than high intensity light of a specific UV wave length band width.

#### SUMMARY OF THE INVENTION:

5

10

15

20

25

. .30

35 Accordingly, the present invention relates to a method of

for determining the authenticity of an ink, which method comprises monitoring the ink for the presence or absence of a marker ingredient in the ink, characterised in that:

- a. the marker ingredient is one which reflects and/or absorbs radiation applied to it within the wave length band width of from 750 to 1500 nanometres and exhibits significant differences in the levels of reflectance and/or absorption of radiation applied to it at at least to 10 predefermed different wave lengths within that range; and in that
  - b. the levels of radiation reflected from and/or absorbed by the ink at the said two wave lengths are monitored and the value of the ratio between the monitored levels is determined and a signal is generated when the ratio departs from a predetermined value.

15

- composition, provides an ink The invention also characterised in that it comprises a marker ingredient whose 20 presence in the composition can be detected, which marker ingredient is characterised in that it exhibits significant differences in the levels of reflectance and/or absorption attack predesermed of radiation applied to it at two different wave lengths within the band width 750 to 1500 nanometres, whereby those 25 levels can be monitored and a ratio determined for those levels.
- The monitoring of the levels can be carried out in situ within the printer itself to ensure that ink being used in the printer is an authentic ink. Alternatively, the monitoring can be carried out on samples of printed images produced by the printer, possibly over a period of time, to ascertain whether the ink applied by the printer to a substrate has been a non-authentic ink. For convenience,

the invention will be described hereinafter in terms of the monitoring of a printed image.

Where the ink is monitored in situ within the printer, similar monitoring techniques may be employed as described below and the printer may incorporate control means which respond to the detection of a non-authentic ink to halt operation of the printer until the non-authentic ink has been purged from the printer so as to reduce potential damage to the printer.

The term authentic ink is used herein to denote an ink which has been manufactured by or an behalf of the printer manufacturer for the printer in which it is being used or which has been manufactured by others to a specification approved by the printer manufacturer. A non-authentic ink is one which has not been so manufactured, even though it may appear to have been manufactured to the required specification. An authentic ink for use in the present invention will also contain the marker ingredient selected by the manufacturer and this will provide a value for the wave lengths at which the radiation or absorption levels are to be determined and the value of the ratios of the values detected at the selected wave lengths which characterise the ink as being an authentic ink as opposed to a non-authentic The printer equipment manufacturer can thus readily determine whether the printer is being operated with a nonauthentic ink and whether this could have given rise to the malfunction which the user of the printer has observed.

30

35

5

10

15

20

25

1.00 M

The marker ingredient for present use can be selected from a wide range of materials which absorb or reflect white light radiation at wave lengths within the specified band width. For convenience, the invention will be described hereinafter in terms of materials which absorb IR radiation. 5

10

15

20

25

30

35

The marker ingredient is one which absorbs IR radiation from radiation, preferably white light, to which it is exposed to different extents at different wave lengths so as to provide reflected radiation which can be monitored at wave lengths in the range 750 to 1500 nanometres. The use of such a selected band width reduces the effects of extraneous visible light or UV radiation on the reflected radiation This reduces the need for corrective being monitored. calibration or software for the monitoring process and enables a simple source of white light to be used to illuminate the marker ingredient. Preferably, the marker ingredient will exhibit at least one peak in its radiation absorption curve, the authentication peak, which is at least 150% greater that the level of absorption at another, reference, wave length. Whilst the separation between the peaks of the authentication and reference wave lengths may be small, problems may be encountered in providing simple, cheap and robust sensors which are capable of operating at small wave length separations. It is therefore preferred that the authentication and reference wave lengths be separated by at least 100 nanometres. It is also preferred that the full width half maximum of the performance curve for the marker ingredient at the peak used for the authentication wave length be less than 200 nanometres, notably about 100 to 120 nanometres, wide.

The marker ingredient is preferably selected so as to provide a ratio of the radiation absorbed or reflected at the authentification and reference wave lengths of at least 1.25:1, preferably 1.5:1, notably 2.0:1, or more.

The marker ingredient may thus be selected from a wide range of materials which have the desired IR absorption patterns. If desired a mixture of marker ingredients may be used to provide a peak at the desired authentication wave length and an enhanced fall or trough at the desired reference wave length. Suitable marker ingredients are available commercially and may be used as such in the ink compositions for present use.

5

10

15

20

35

The ink composition may be a solvent based composition using, for example, an aliphatic ketone and/or alkanol as the solvent, or may be a water based ink; and the marker selected to be soluble, miscible ingredient is dispersible in one or more of the other ingredients of the Whilst the marker ingredient may be ink composition. present in the form of a particulate solid, for example as a pigment in a hot melt ink composition, it will usually be preferred that it is soluble in the ink composition. desired, the marker ingredient may be subjected to pretreatment, for example emulsification or dispersion in an oil carrier for an oil or solvent based ink, or acylation or esterification for a water based ink, to render compatible with the ink composition. Alternatively, a cosolvent or bridging solvent may be used to assist incorporation of the marker ingredient into the ink composition and the stability of the ink composition during storage and use.

The marker ingredient will usually be present in the ink composition in the minimum amount required for detection by the monitoring equipment used. Typically, the marker ingredient will be present in less than 5% by weight of the ink composition, preferably from 0.05 to 1%. As indicated above, the marker ingredient may be a mixture of materials and the above figure represents the total amount of such a mixture present. However, where the marker ingredient exhibits two properties, both of which are being monitored, this may be achieved by the presence of two different

ingredients and the above figures relate to each such

ingredient. Thus, for example, one ingredient may exhibit a peak IR absorption at a wave length of about 850 nanometres and another ingredient exhibits a peak IR absorption at a wave length of about 1150 nanometres; and authentification of the ink is based upon the ratio of the levels detected at these peaks. In this case, it will usually be desired to have the above amounts of each of the IR absorbing materials in the ink composition to provide a mixed marker ingredient for present use.

10

15

20

25

30

35

5

The invention has been described above in terms of the use of a material or mixture of marker ingredients which exhibit absorption or reflection at two distinctive wave lengths. However, it will be appreciated that marker ingredients which exhibit absorption and/or reflectance at more than two characteristic wave lengths may be used. The authentification of inks containing such marker ingredients would then be based on the ratio of the levels detected at two or more of the characteristic wave lengths. It is also within the scope of the present invention to use mixtures of marker ingredients and to carry out the authentification on one or more of the levels from two different ingredients in the mixture. For convenience, the invention will be described hereinafter in terms of the use of a single marker ingredient having two characteristic wave lengths.

The marker ingredient can be incorporated into the ink composition at any suitable point during or after the manufacture of the ink using any suitable technique. If desired, it can be incorporated into one of the components of the ink composition before that is incorporated into the ink composition.

The ink composition can be used in a wide range of types of printing process, for example in a contact printing process,

for example a gravure, offset, letterpress or other printer in which ink is applied by being applied by a plate or roller which then applies the ink to the substrate to be printed. However, the invention is of especial benefit in inks for an ink jet printer where the ink is applied as a series of discrete droplets to a substrate to form the desired image on the substrate. For convenience, the invention will be described hereinafter in terms of the use of an ink jet printer to apply the ink.

10

15

20

25

30

35

5

The presence or absence of the marker ingredient can be detected at any suitable point in the ink flow path during operation of the printer and the absence of the marker ingredient used to shut down operation of the printer before any significant damage is caused to the printer equipment. Thus, for example, a suitable sensor can be mounted adjacent the ink reservoir of the printer to monitor the ink in the reservoir; or a sensor can be located adjacent the nozzle orifice of the printer to monitor the ink as it flow through the ink flow lines feeding the print head or the droplets of ink as they issue from the nozzle orifice. The sensor can monitor the reflectance of radiation from a surface of the ink, as when a sensor scans the surface of the ink in the Alternatively, the sensor can monitor the reservoir. absorption of radiation by the ink, as when IR radiation is passed through a glass or other IR translucent window or wall of a vessel containing the ink or a conduit through which the ink is flowing and the sensor monitors the radiation passing through the ink in the vessel or conduit from the opposite side of the vessel or conduit. desired, the sensors can serve dual functions, for example both as level sensors for the reservoir or droplet detectors in time of flight monitors and the like and as IR sensors. If desired, the sensors can be provided with optical and/or electronic filters to enhance the selectivity of the wave

lengths to which the sensor responds or separate sensors can be used to monitor the separate authentification and reference wave lengths of the radiation from the ink.

Alternatively, the presence or absence of the marker 5 ingredient can be monitored in the ink image formed on a In this case, it will be substrate by the printer. appreciated that the image can be examined some long time after the image has been formed. For example, the image may 10 be inspected some days or weeks after the image has been printed and at a location removed from the printer, as when a code on a package is examined at a user or distributor's warehouse. For convenience, the invention will be described in terms of examination of a printed image carried out at a 15 time and location separated from the operation of the printer.

> The image can be examined by any suitable means to detect the presence or absence of the marker ingredient. Thus, the image is illuminated with white light containing components within the 750 to 1500 nanometre wave band width and the authentication and reference values determined from the IR radiation reflected from the image. However, since been selected marker ingredient has authentication and reference wave lengths in the range 750 to 1500 nanometres, it is possible to illuminate the ink or image with ordinary white light and it is not necessary to use specific wave length illumination sources or high intensity radiation to excite the marker ingredient. It is particularly preferred that the image is illuminated by a The term white light is collimated beam of white light. used herein to include all illumination sources which emit light which contains components within the 750 to 1500 nanometre wave length band width.

20

25

30

5

10

15

20

35

4

The reflected light is then monitored by a suitable optical scanner to detect the intensity of reflectance at the desired wave lengths. If desired, sensors which respond to the specific desired wave lengths can be employed. However, we have found that such sensors often respond to light over a comparatively wide wave length and cannot accurately discriminate between the authentication and reference wave lengths unless these have widely separated wave lengths. This may exclude the use of many IR absorbent materials which would otherwise be suitable and thus limit the application of the invention. It is therefore preferred to use filters to select the desired wave length radiation from the white light reflected from the image. Such filters can be made to select narrow bands of radiation, thus enabling closely related authentification and reference wave lengths to be used. The filters are preferably optical filters which remove substantially all but the desired wave length from the white light reflected from the image. Typically, two wave lengths will be selected, but the use of filters enables an operator to select more wave lengths if desired so as to increase the discrimination of the sensor and/or to accommodate where the image exhibits more than two distinctive wave length radiation absorptions.

We believe that scanners incorporating two filters to enable the scanner to discriminate between two wave lengths of the white light illumination reflected from the printed image are novel. The invention therefore also provides apparatus for monitoring the reflectance of white light from a surface having an image printed thereon of an ink of the invention, which apparatus comprises:

- a. a source of illumination adapted to direct white light onto the image to be scanned; and
- b. means for monitoring the reflected light from the image; and

5

10

15

- c. two or more filters adapted to be located between the said image and the said means, which filters are adapted to absorb or transmit at least part of that light reflected from the said image which has a wave length corresponding to the authentification or reference wave length; and
- d. means, for example electronic and/or microprocessor means, adapted to establish the relative intensities of the illumination reflected from the said image at the authentification and reference wave lengths.

The ability to use white light to illuminate the image simplifies the apparatus for present use, yet the use of authentification and reference wave lengths within the range 750 to 1500 nanometres reduces the effect of extraneous reflected visible light or UV radiation on the detection of the marker ingredient.

20 The image can be of a wide range of forms, but will often be in the form of a bar code or the like which can be scanned by any suitable optical device. For example, the image can be scanned by a device which is commercially available as a bar code scanner, with suitable modification of the receptor 25 sensor and/or the provision of suitable optical filters, to monitor the reflected light at the desired wave lengths. Alternatively, the monitoring control can be achieved by suitable software in the scanner control means. particularly preferred form of scanner is one in which 30 illuminating white light is collimated and passed through a ball type lens which also serves to receive any radiation reflected from the surface of the image so that small areas of the image can be scanned and the scanner can be operated by sweeping the scanner tip across the printed image. scanning 35 devices can readily be manufactured

conventional electronic designs, components and techniques or by modification of existing devices to accommodate the specific wave lengths required for the authentication and reference monitoring. If desired, the scanning devices may incorporate security features so that they can only be accessed by authorised personnel.

5

10

15

20

25

30

35

The levels of radiation detected by the sensors at the authentification and reference wave lengths can be processed in any appropriate manner to determine the ratio between the two levels. This processing is conveniently achieved using conventional electronic means and may be carried out on a continuous or intermittent basis where the monitoring in carried out in situ during the operation of the printer. If desired, the ratio of the authentification to reference radiation values may be assessed on several images and an average taken, as when the images formed on a moving article such as a package are scanned continuously.

As stated above, we have found that the ratio between the authentification and reference light values is remarkably consistent for a given ink composition and marker ingredient and deviation of the ratio from the expected value enables an operator of the printer or inspection of the printed image to determine whether the ink is authentic or not. Where the ratio falls outside a permitted deviation from the expected value, for example  $\pm$  10%, means can be provided to alert the operator or inspector of this. For example, electronic or other means can be provided for halting operation of the printer and for initiating flushing of the ink flow lines of the printer to purge the printer of nonauthentic ink if excessive deviation from the expected ratio Where the printed image is being scanned, the occurs. scanner can provide an audible and/or visible signal to alert the inspector to a non-authorised ink. If desired,

means can be provided for providing a record of the values of the ratios observed, for example so as to provide a record of the operation of the printer over a period of time for future reference in the event of a malfunction of the printer.

5

10

The method and apparatus of the invention thus enable a printer manufacturer to ascertain whether a malfunction is due to non-authorised ink being used in the printer and enables a user to stop operation of a printer as soon as practicable once the use of non-authorised ink within the ink flow system of the printer has been detected, thus reducing the risk of damage to the printer.

#### CLAIMS:

. . . . . .

- A method for determining the authenticity of an ink, which method comprises monitoring the ink for the presence or absence of a marker ingredient in the ink, characterised in that:
- a. the marker ingredient is one which reflects and/or absorbs radiation applied to it within the wave length range of from 750 to 1500 nanometres and exhibits significant differences in the levels of reflectance and/or absorption of radiation applied to it at at least to prodefermine different wave lengths within that range; and in that
- b. the levels of radiation reflected from and/or absorbed by the ink at the said two wave lengths are monitored and the value of the ratio between the monitored levels is determined and a signal is generated when the ratio departs from a predetermined value.
  - 2. A method as claimed in claim 1, characterised in that the radiation is applied to the ink in a printed image.
- 3. A method as claimed in claim 1, characterised in that radiation is applied to ink in the ink flow path of the ink jet printer.
- 4. A method as claimed in any one of the preceding claims, characterised in that the radiation is white light and optical means are used to detect the radiation at two wave lengths reflected and/or absorbed by the ink.
- 5. A method as claimed in claim 4, characterised in that the two wave lengths being monitored differ from each other

by at least 100 nanometres.

5

10

. . . . . .

Tanking has a

- 6. A method as claimed in any one of the preceding claims, characterised in that the ratio of the levels of radiation monitored at said two wave lengths is at least 1.25:1.
- 7. A method as claimed in any one of the preceding claims, characterised in that the ink is illuminated with white light and the reflected light is passed through one or more filters to enhance the selectivity of the sensor in monitoring the desired wave lengths in the reflected light.
- 8. A method as claimed in claim 1, characterised in that the ratio is monitored in respect of moving printed images or in respect of ink flowing within the ink flow system of an ink jet printer, and the monitoring is carried out on an intermittent or continuous basis.
- 9. An ink composition, characterised in that it comprises
  20 a marker ingredient whose presence in the composition can be
  detected, which marker ingredient is characterised in that
  it exhibits significant differences in the levels of
  reflectance and/or absorption of radiation applied to it at allegation of the production of the produc
- 10. An ink composition as claimed in claim 9, characterised in that the marker ingredient is a material which absorbs infra red radiation in the wave length range 750 to 1500 nanometres.